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Synthesis of N,N'-Disalicylidene-ethylenediamine(Salen)-Porphyrin Combined System with Constrained Conformations

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Salen-capped porphyrin and salen-bridged porphyrin dimer as well as their zinc and nickel complexes were synthesized. In the capped complex, the nickel-salen moiety was rigidly held over the porphyrin ring, while preferred conformations of salen-bridged porphyrin dimers were controlled by the metal complexation.

Extensive studies of binuclear metal complexes have been made in recent years as simple chemical models for biological metalloproteins containing bimetallic centers.[1] One of the important requirements for the model complexes is the close proximity of two metal centers in a well-defined three dimensional geometry, as such in biological systems. Key roles of hemoproteins and porphyrin pigments in biological systems provide impetus for the construction of binucleating porphyrins such as porphyrin dimers,[2] porphyrin-crown ether,[3] and porphyrin-bipyridine.[4] However, the metal combinations of these homo- and hetero-binucleating porphyrin ligands were rather limited and the geometrical relationship of the metal centers were not clear in most cases.

Now we wish to report the synthesis of a novel salen-porphyrin combined system with constrained conformations. The bis-salicylaldehyde-linked porphyrin 1 , which was synthesized by the reaction of didodecyl substituted porphyrin diacid chloride 2 [5] with 2-hydroxy-5-(2-hydroxyethyl)benzaldehyde (3) [6] in 75% yield, was condensed with 1.2 equimolar amounts of 1,2-ethylenediamine in CH_2Cl_2 at room temperature. After 72 h, most of the original porphyrin 1 was converted to the salen-capped porphyrin ($SCP(H_4)$) 4. Evaporation of the solvent followed by addition of methanol induced the precipitation of pure $SCP(H_4)$ (4: mp 95-97 °C) in 75% yield. Similarly, salicylaldehyde-linked porphyrin 5 reacted with 0.6 equimolar amounts of 1,2-ethylenediamine in CH_2Cl_2 for 24 h to furnish 6 $PSP(H_6)$ (mp 168-170 °C) in 95% isolated yield.[7]

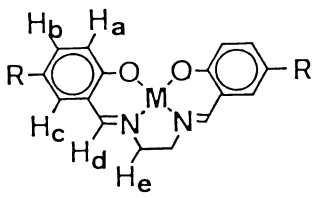
Treatment of 6 with nickel(II) acetate in CH_2Cl_2 at room temperature resulted in the insertion of nickel(II) only to the salen site of 6, giving 7 $PSP(H_4Ni)$ (mp 195-197 °C), which was transformed into the hetero-metal complex 8 $PSP(Zn_2Ni)$. Similar treatment of 4 $SCP(H_4)$ gave rise to the formation of 9 $SCP(NiH_2)$. Under refluxing conditions in $CHCl_3$, 6 was converted into the trinickel complex 12 $PSP(Ni_3)$. Schiff base condensation of the salicylaldehyde-linked zinc-porphyrin 10 with 1,2-ethylenediamine gave rise to the formation of 11 $PSP(Zn_2H_2)$ (mp 136-139 °C), which was also converted to 8.

The ^{1}H-NMR spectra of these complexes showed high field shifts of the salen protons due to the porphyrin ring current, which depended upon the ligand structure and the complexed metals (Table 1). Among these, the protons of the nickel-salen moiety in 9 SCP(H_4) appeared in the highest field, although its extremely broadened ^{1}H-NMR spectrum, suggesting strongly a rigidly constrained conformation of the salen-cap, prevented the unambiguous assignment of H_d and H_e. Greatly reduced fluorescence intensity of 9 is apparently due to the intramolecular porphyrin fluorescence quenching by the nickel-salen moiety in close proximity (Table 2). Similar but slightly less high field shifts of the nickel-salen moiety were observed in 7 PSP(H_4Ni), indicating the folded conformation of the nickel-salen moiety over the porphyrin macrocycle, as shown in Fig. 1a. Reduced fluorescence intensity of 7 was consistent with the suggested conformation. On the other hand, the high field shifts of the nickel-salen protons were relatively small in 8, while the meso-protons of the zinc-porphyrin moieties of 8 and 11 were markedly shifted to the higher region. These facts suggested that in the bis-zinc-porphyrin complex 8 interaction between two zinc-porphyrin ends was stronger than that between zinc-porphyrin and nickel-salen, which resulted in the different folded conformation depicted in Fig. 1b. Electronic interaction between the two zinc porphyrin ends were also realized by their absorption spectra, in which Q-bands were red-shifted. The fact that the fluorescence intensities of 8 and 11 were similarly reduced despite the presence

Table 1. ^{1}H-NMR Data for Porphyrin-Salen Compounds in $CDCl_3$

Compound		Chemical shift δ / ppm								
		H_a	H_b	H_c	H_d	H_e	meso-H			
4	SCP(H_4)	6.67	6.85	6.56	7.56	3.17	9.96			
6	PSP(H_6)	6.63	6.80	6.50	7.46	3.08	10.03	10.02	10.01	10.00
11	PSP(Zn_2H_2)	5.96	6.79	6.34	7.42	3.36	9.33	9.26	9.17	9.13
	13	6.89	7.14	7.06	8.30	3.93				
9	SCP(NiH_2)	6.30	6.61	5.84	a)	a)	9.73			
7	PSP(H_4Ni)	6.64	6.77	6.03	5.26	0.17	10.06	10.05	10.02	9.99
8	PSP(Zn_2Ni)	6.60	6.93	6.47	6.36	2.56	9.24	9.22	9.15	9.08
12	PSP(Ni_3)	6.79	6.72	6.00	6.06	1.55	9.76	9.71	9.70	
	14	6.97	7.06	6.89	7.48	3.41				
	16							10.09	10.07	
	17							9.93	9.91	

a) Not characterized.

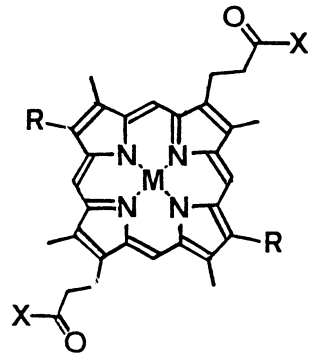


13; M=H_2, R=CH_2CH_2OAc
14; M=Ni, R=CH_2CH_2OAc

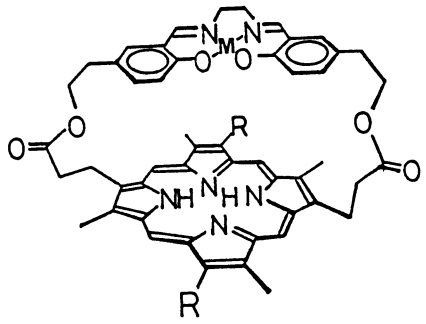
Table 2. Absorption and Fluorescence Spectral Data

Compd.	λmax / nm					$\Phi f^{a)}$ (λEm_{max}/nm)
	Soret	Q-bands				
4	398	498	536	571	622	0.56[b] (620)
9	401	502	536	568	621	0.074[b] (620)
15	399	499	536	568	620	1.0 (619)
6	398	499	532	567	620	0.88[b] (620)
7	398	498	533	566	620	0.28[b] (619)
16	398	498	533	566	620	0.91[b] (620)
11	401		534	572		0.36[c] (570)
8	403	412	538	573		0.34[c] (571)
17	401		531	568		1.0 (570)

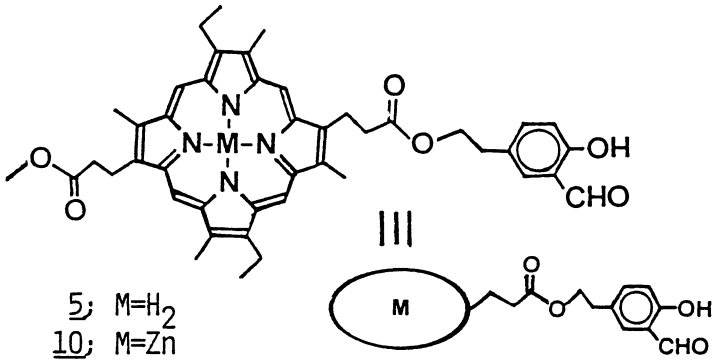
a) Relative fluorescence intensities in CH_2Cl_2 at 25 °C. Excitation at Soret wavelength.
b) Relative to 15.
c) Relative to 17.



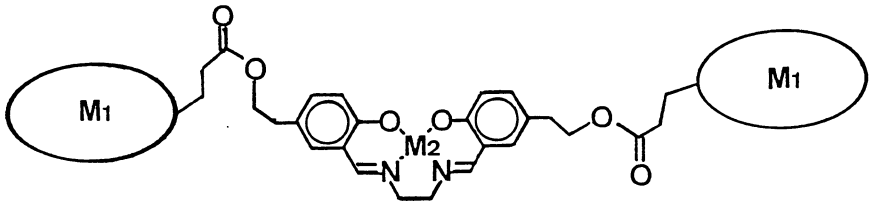
15; R=$C_{12}H_{25}$, X=OMe, M=H_2
16; R=Et, X=OMe, M=H_2
17; R=Et, X=OMe, M=Zn
1; R=$C_{12}H_{25}$, M=H_2
X=OCH_2CH_2-(OH, CHO)
2; R=$C_{12}H_{25}$, X=Cl, M=H_2



4 SCP(H_4); M=H_2
9 SCP(NiH_2); M=Ni



5; M=H_2
10; M=Zn



6 PSP(H_6); M_1=M_2=H_2
7 PSP(H_4Ni); M_1=H_2, M_2=Ni
8 PSP(Zn_2Ni); M_1=Zn, M_2=Ni
11 PSP(Zn_2H_2); M_1=Zn, M_2=H_2
12 PSP(Ni_3); M_1=M_2=Ni

of the nickel-salen bridge in 8, provided a support for a preferred interaction of the two zinc-porphyrin ends.

As demonstrated above, the salen-porphyrin combined ligands 4 and 6 conveniety gave us heteronuclear metal complexes. The nickel-salen moiety was rigidly held over the porphyrin ring in the salen-capped porphyrin 9, while the conformations of the salen-bridged porphyrin dimers were controlled by the metal complexation; the porphyrin-nickel-salen interaction was strong in 7, but the interaction between the zinc-porphyrin ends was preferred in 8 and 11.

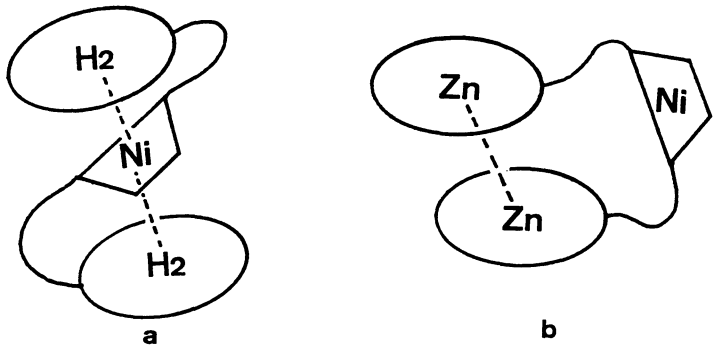


Fig.1. Proposed conformations of 7 (a) and 8 (b).

References

1) D.E.Fenton, "Do Binucleating Ligands have a Biological Relevance ?," in "Advances in Inorganic and Bioinorganic Mechanisms," ed by A.G.Sykes, Acad. Press (1983), Vol.2, pp.187-257.

2) S.S.Eaton, G.R.Eaton, and C.K.Chang, J.Am.Chem.Soc., 107, 3177 (1985) and references cited therein.

3) a) C.K.Chang, J.Am.Chem.Soc., 99, 2819 (1977); b) V.Krishna, ibid., 104, 3463 (1982); A.Hamilton, J.M.Lehn, and J.L.Sessler, ibid., 108, 5158 (1986); N.M.Richardson, I.O.Sutherland, P.Camilleri, and J.A.Page, Tetrahedron Lett., 26, 3739 (1985).

4) A.D.Hamilton, H.D.Rubin, and A.B.Bocarsly, J.Am.Chem.Soc., 106, 7255 (1984).

5) Didodecyl substituted porphyrin was prepared by the similar method given in Chang's procedure, see Ref.3a.

6) Aldehyde 3 was prepared in three steps from commercially available 4-hydroxyphenethyl alcohol. (overall yield, 45%): ^{1}H-NMR($CDCl_3$) δ=10.89(1H,s), 9.87 (1H,s), 7.43-7.39(2H,m), 6.95(1H,d,J=8.3 Hz), 3.87(2H,t,J=6.4 Hz), 2.86(2H,t, J=6.4 Hz); MS m/z 166(M^+).

7) Porphyrin 5 was prepared by the reaction of mesoporphyrin II monoacid chloride with 3 in CH_2Cl_2 in 75% yield.

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